

From this we may draw the conclusion, that either the materials of the earth have about the strength of granite at 1,000 miles from the surface, or they have a much greater strength nearer to the surface.

This investigation must be regarded as confirmatory of Sir William Thomson's view, that the earth is solid nearly throughout its whole mass. According to this view, the lava which issues from volcanoes arises from the melting of solid rock, existing at a very high temperature, at points where there is a diminution of pressure, or else from comparatively small vesicles of rock in a molten condition.

XIX. "On the Refraction of Electricity." By ALFRED TRIBE, F.I.C., Lecturer on Chemistry in Dulwich College. Communicated by Dr. GLADSTONE, F.R.S. Received June 7, 1881.

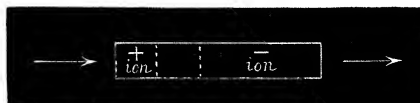
On December 15, 1880, I had the honour of communicating to the Royal Society the latest results of my work on electric distribution. In that paper there is included a description of results which form the basis of a graphic and electro-chemical method of investigating the field of electrolytic action. These results may be classed under three heads:—1st. Distribution of electricity on metallic conductors in electrolytic media. 2nd. Physical differences in corresponding parts of non-homogeneous electrolytic fields. 3rd. Direction in which the energy is transmitted.

As the detailed account of these experiments has not yet been published, it is necessary for the appreciation of the evidence to be adduced to give in this place the groundwork of that part of the method relating to the direction in which the energy is transmitted. It will be convenient to do this under three heads. Let it be remembered that a rectangular electrolytic cell was used, that the electrolyte was a solution of copper sulphate, and the electrical relations of the liquid were ascertained by immersing in it a rectangular silver plate (called an *analysing plate* or *analyser*), on which the ions were deposited. In all cases the positive ion separates and is distributed on that part of the plate which may be supposed to receive — electrification, or by which the + energy enters the analyser, while the — ion separates on that part of the same plate which receives + electrification, or from which the energy emerges.

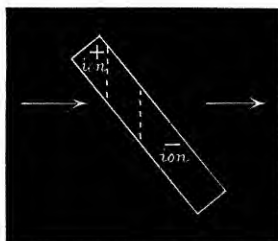
$\alpha$ . When the course of the energy\* is parallel with any two edges of an analyser, and therefore with the sides, the boundary lines of the ions on both sides of the plate are parallel with the plane of the elec-

\* I assume that the energy in a homogeneous field runs in straight parallel lines from one electrode to another, and that this course is not appreciably disturbed by an analyser.

trodes, and consequently perpendicular to the direction of the influence. Distributions having these characteristics are named *parallel*. The dotted lines in the figure represent the boundary lines and the arrows the course of the energy.



$\beta$ . When the course of the energy is parallel with the sides of an analyser, but makes with its edges an oblique angle, the boundary lines of the ions are still parallel with the plane of the electrodes, but necessarily cross the sides of the plate obliquely to its edges. This obliquity varies proportionately with the angle of inclination of the analyser to the energy, so that in all cases the boundary lines are perpendicular to the direction of its transmission.



$\gamma$ . When the course of the energy makes an oblique angle with the sides of the analyser, neither the magnitude nor the boundary configuration of the same electrification is identical on the two sides of the plate. The boundary of the positive ion on the side in opposition to the direct course of the influence is now markedly *convex*, and greater in magnitude than on the reverse side, where, moreover, the boundary configuration of the same ion is markedly *concave*. Again, the boundary line of the negative ion on the first-named side of the analyser is *concave* and smaller in magnitude than on the reverse side, where the boundary of this ion is *convex*. The convexity and concavity of these several boundaries increase as the direction of the energy approaches a perpendicular to the sides of the analyser. Both the classes of distributions described in  $\beta$  and  $\gamma$  are named *non-parallel*.

The position of the ions on an analyser, and the character of their boundary lines determine then, and with accuracy, the direction of the energy in the electrolytic field relatively to either side or edge of the analysing plate.

Many questions have occurred to me in the investigation of which this method might be expected to afford material assistance. But the one of immediate attraction was whether electricity is endowed, like light, heat, and sound, with the quality of refraction. From the general resemblance of the fundamental laws of the forms of energy, I instituted experiments in the expectation of finding an answer in the affirmative to this question, the better conducting electrolytic medium being taken as the electric analogue of the more rare medium in light.

### *Refraction.*

My first trials were made with double convex-shaped bladders. These gave what I took to be a slight evidence of refraction, though the result was far from satisfactory. Triangular-shaped cells were next employed, made by placing diaphragms of parchment-paper obliquely across the electrolytic cell near its ends. In this way unmis-takeable proof was obtained of the bending of the energy in passing the line of demarcation of the two media. When the influence passed from one medium to the other perpendicularly, *i.e.*, when the diaphragms were parallel to the plane of the electrodes, no refraction whatever took place.

On further consideration the arrangement which appeared less open to objection, and at the same time the most simple and theoretically the best, was a *refracting cell*, having parallel sides of some material permeable to the electric influence. In the first instance parchment-paper was the material employed. Two sheets of this substance were fixed in a vertical position across an electrolytic cell, 380 millims. long, 128 millims. broad, and 128 millims. deep, at an angle of  $45^\circ$ . They were parallel to one another, 76 millims. apart, but equidistant from the respective ends of the cell.

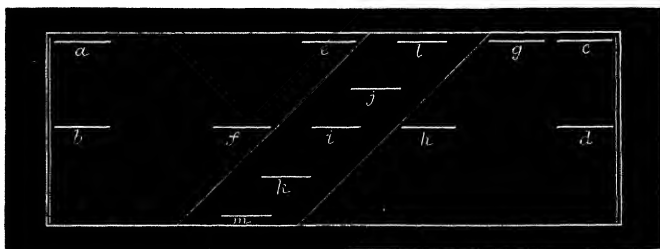
An unit current was employed, and copper electrodes of the breadth and depth of the outer or transmitting cell. A 1 per cent. solution of copper sulphate was placed in the inner or refracting cell, and a concentrated solution of the same salt in the transmitting cell. On placing successive analysers\* lengthwise in several parts of the *central line* joining the electrodes, parallel distributions were recorded by all the plates in the transmitting cell, but the one in the refracting cell recorded a non-parallel distribution of a most pronounced character, and it was evident from the degree of curvature of the ions that the course of the energy on passing into the medium of less conductivity, had bent out of its original course some  $20^\circ$ .

The difficulty of keeping the parchment diaphragms as rigid as was necessary for a more extended study of this phenomenon of refraction

\* Unless the contrary is stated, it is to be understood that analysers  $40 \times 7$  millims. were used, and placed in the electrolyte with their shorter edges upright.

led to their substitution by others of unglazed earthenware. These consisted of the sides of a large rectangular porous cell ground to as uniform a thickness as possible. With this alteration, but with all the other above-mentioned conditions, the following experiments were made.

Analysers were successively placed in the positions (all perpendicular to the electrodes) shown in the annexed diagram, exhibiting a horizontal section drawn to about one-fifth the scale.



The analysers *a*, *b*, *c*, *d*, 2 millims. from electrodes, recorded parallel distributions.

The analysers *e*, *f*, *g*, *h*, 2 millims. from diaphragm, recorded not absolutely but very nearly parallel distributions. This slight non-parallelism was not noticed in the analogous experiment with the parchment diaphragms, and I am disposed to attribute it to a greater diffusion in this case occasioning a less sharp line of demarcation between the media.

The analyser *i*, midway between the diaphragms, recorded a non-parallel distribution of a most pronounced character. The degree of curvature showed that the energy had been refracted through some  $30^\circ$ , while the position of the ions proved that the bending was towards a perpendicular to the refracting surface. Furthermore, the symmetry of the curve showed that the plane of refraction was the same as that of the incident energy.

The analysers *j*, *k*, indicated a result almost identical with *i*.

The analysers *l*, *m*, showed a much smaller deviation from the original course of the energy.

The positions of the relatively good and bad conducting media were now reversed. The 1 per cent. solution was placed in the transmitting cell, and the concentrated in the refracting cell. An analyser at *i* recorded a non-parallel distribution, and the curvature and position of the ions showed that the course of the energy had been bent about  $15^\circ$ . But in this case the refraction was *from* a perpendicular to the refracting surface.

It was now natural to anticipate that the refraction, with a given

incidence, would decrease or increase as the media in the refracting and transmitting cells approached or receded in conducting power. This was proved to be the case, first, by replacing the 1 per cent. solution of copper sulphate in the refracting cell by a 2, 3, 5, and 10 per cent. solution respectively, when analysers at  $i$  recorded respectively a decreasing refraction as the media in the cells approached equality. And, secondly, by placing a 5 per cent. solution of copper sulphate in the refracting cell, and successively a concentrated solution of copper sulphate, a concentrated solution of sodium chloride, and a dilute solution (1—11) of oil of vitriol in the transmitting cell. Analysers at  $i$  showed, in the case of the copper sulphate, a refraction of about  $15^\circ$ , in the case of the sodium chloride,  $30^\circ$ , and in that of the dilute sulphuric acid,  $40^\circ$ . The order of the increase in refraction is here the same as that of the conductivities of the liquids.

Again, it was anticipated that the refraction would decrease as the incidence decreased. This was proved to be true by setting the diaphragms so that the angle of incidence should be  $45^\circ$ ,  $30^\circ$ , and  $15^\circ$  respectively. With a 5 per cent. solution of copper sulphate in the refracting cell, and dilute sulphuric acid in the transmitting cell, a refraction of about  $35^\circ$  was obtained when the incidence was  $45^\circ$ , about  $22^\circ$  when at  $30^\circ$ , and about  $7^\circ$  when at  $15^\circ$ .

#### *Relation between Electric Incidence and Refraction.*

That part of the electro-chemical method which has been already described supplies three means of determining the bending of the course of the energy on its passage into the refracting cell. First, by the curvature of the ions on an analyser with the shorter edges of the plate upright, and its length perpendicular to the electrodes. But the practical impossibility of obtaining accurate measurements of these curves, renders this plan only roughly quantitative. Secondly, by placing an analyser at various angles to a right line joining the electrodes, until it records a *parallel* distribution. This is the case when the course of the energy is parallel with the sides of the analysing plate, and the angle enclosed between the plate and the right line referred to consequently expresses the amount of refraction. The objections to this plan are twofold. It is very tedious, and it is also difficult to determine with sufficient accuracy the angle of the plate as it stands in the cell. The refraction numbers given above were obtained by this second method, and for the last of the reasons just mentioned I regard them only as approximately correct. The third plan, based on the fact that the course of the influence, when parallel to the sides of an analyser, is perpendicular to the boundary lines of the ions set free, is the one I have employed for the more accurate determination of the relation between electric incidence and refraction.

I employed for this purpose four similar electrolytic cells of the shape and dimensions given in p. 436. Pairs of porous plates were set across each of these cells, as before described, so as to give in one case an incident angle of  $45^\circ$ ; in the second,  $37\frac{1}{2}^\circ$ ; in the third,  $30^\circ$ ; and in the fourth,  $15^\circ$ . Dilute sulphuric acid (1 to 11) was used in the transmitting cell, and a 5 per cent. solution of copper sulphate in the refracting cell. The current generally used was three Webers, though variations in this respect were found not to affect the refraction. The time of each determination was five minutes. The analysers employed were squares (24 millims. the side) of sheet silver, and disks of the same material 24 millims. in diameter. These were immersed horizontally in the centre of the refracting cell, the squares in such a way that their edges were parallel with the respective sides and ends of the rectangular electrolytic cell; the disks, so that a line passing through their centres was coincident with a line joining the electrodes.

As it has been already shown that the course of the energy in the transmitting and refracting cells was in the same horizontal plane, it was to be anticipated that the boundary lines of the ions on the analysers placed in the positions just described would be straight. Such is the case with the boundary of the negative ion, which consequently is taken for purposes of measurement.

Were the course of the energy in the inner cell identical with that in the transmitting cell, the boundary lines, in accordance with the rule in  $\beta$ , would be perpendicular to a right line joining the electrodes, and this might be named the zero line, or line of no refraction. And were the analysers in the position described, the zero line would be perpendicular to the central line on the disks and to the edges of the squares, which are parallel with the sides of the cell. It follows that, were the course of the energy diverted from a right line joining the electrodes (its original course), the boundary line of the ion would deviate *pari passu* from the line of no refraction. The numbers expressing this obliquity or amount of refraction in five series of trials are given in the annexed table. In Series I, II, III, square analysers were used, and for IV and V the disks already described.

Angle of incidence.	Deviation.				
	I.	II.	III.	IV.	V.
$15^\circ$	$9^\circ$	$9^\circ$	$9^\circ$	$10^\circ$	$9^\circ$
$30^\circ$	19	20	19	19	20
$37\frac{1}{2}^\circ$	27	26	25	26	25
$45^\circ$	31	31	33	33	32

These data give the following ratios between the angles of incidence and refraction—

$$\frac{i}{r}.$$

I.	II.	III.	IV.	V.
2·5	2·5	2·5	3·0	2·5
2·7	3·0	2·7	2·7	3·0
3·5	3·3	3·0	3·3	3·0
3·2	3·2	3·7	3·7	3·4

and the following ratios between the sines of the angles of incidence and refraction—

$$\frac{\sin i}{\sin r}.$$

I.	II.	III.	IV.	V.
2·5	2·5	2·5	2·9	2·5
2·6	2·8	2·6	2·6	2·8
3·3	3·0	2·8	3·0	2·8
2·9	2·9	3·4	3·4	3·1

Taking the results as they thus appear, I think they justify the conclusion that the more probable relation between electrical incidence and refraction is as the sines of their respective angles. And further, as the experimental difficulties are overcome and the inherent sources of error appreciated, this relation may be still more rigidly found to obtain.

This electro-chemical method being new, it would be well to supplement, if possible, the evidence it has furnished of the laws of electric refraction by one based on more familiar principles. I am engaged in perfecting a method founded on those employed by De la Rive in 1825, and by Professor Adams in 1875, for investigating the laws of electric distribution in electrolytes, which I have reason to believe will demonstrate in another way the main facts set forth in this communication.

#### *Conclusions.*

I. Electricity passes without alteration of direction from one electrolytic medium to another differing from it in conductivity, when the course is perpendicular to the surfaces of contact.

II. Electricity, on passing obliquely from one medium to the other,

suffers refraction, and in the same plane; towards the perpendicular, when from a better to a worse conductor, and from the perpendicular when from a worse to a better conductor.

III. The refraction increases or decreases as the media recede from or approach one another in conductivity.

IV. The refraction increases as the incidence increases.

[NOTE.—It is known that the flow of electricity in an electrolyte follows the same laws as the flow of heat in a conductor when the condition has become permanent. It readily follows, that when two electrolytes of different specific resistance, suppose a strong and a weaker solution of sulphate of copper, are in contact, a change in the direction of the flow takes place in passing out of the one into the other.

Let  $v$  be the potential in the first medium,  $i$  the angle of incidence, or in other words, the inclination of the tangent plane at any point in the surface of separation to the tangent plane to the equipotential surface in the first medium which passes through the same point,  $c$  the specific conducting power,  $ds$  an element of a section of the common surface by the plane of incidence,  $dn$  an element of a normal to the equipotential surface,  $f$  the flux of electricity, and let  $v'$ ,  $i'$ ,  $c'$ ,  $dn'$ ,  $f'$ , be for the second medium what  $v$ ,  $i$ ,  $c$ ,  $dn$ ,  $f$  are for the first. Then we have

$$f = c \frac{dv}{dn} = c \operatorname{cosec} i \frac{dv}{ds}, \quad f' = c' \operatorname{cosec} i' \frac{dv'}{ds}.$$

But if we take an elementary closed curve in the surface of separation, and make it the base of elementary tubes in the two media bounded by lines of flow, since the same quantity of electricity must flow through the two tubes, and the areas of their sections are as  $\cos i$  to  $\cos i'$ , we have

$$f \cos i = f' \cos i',$$

and eliminating  $f/f'$  between these two equations, we get, since  $v = v'$  and therefore  $dv/ds = dv'/ds$ ,—

$$\tan i' = \frac{c'}{c} \tan i,$$

so that according to theory the tangents, not sines, of the angles of incidence and refraction are in a given ratio.

If the potentials in the two media, instead of being equal at the surface of separation, differ by a constant quantity, as may conceivably be the case when the two electrolytes are different in nature, so that different chemical actions go on in them, the above relation would not be disturbed.

The results obtained by Mr. Tribe agree rather better with the law of sines than with the law of tangents. But several circumstances



tend to introduce greater or less errors. For example, the flow in the second medium must have been somewhat disturbed by the circumstance that the non-conducting walls of the intermediate cell were parallel to the direction of the incident, not refracted flow, which may possibly have disturbed the course even as far as the middle of the cell. Again, there would have been a much larger resistance in the porous wall than in a stratum of equal thickness of one of the electrolytes, and the thickness or porosity of the wall, or the proportion of the two electrolytes imbibed by it, may have varied somewhat in a lateral direction. The numbers obtained cannot therefore be deemed sufficient to decide between two such laws as that of sines and that of tangents. In case of the second medium being the better conductor, it is evident that the law of sines would lead to extravagant results, as there can be no such thing as total internal reflection. The alteration in the direction of the equipotential surfaces, and, therefore, of the lines of flow, in passing from one metal into another of different conducting power, has already been investigated experimentally by Quincke, and the results of experiment compared with theory. ("Pogg. Ann.," vol. xcvii [1856], p. 382.)—G. G. S., 14 June, 1881.]

XX. "Note on the Spectrum of Sodium." By Captain W. de W. ABNEY, R.E., F.R.S. Received June 14, 1881.

On examining the spectra of different metals, there is one point which is striking in the extreme, viz., the absence of any very marked lines in the region between  $\lambda$  7000 and  $\lambda$  7600, which latter number we may take as the visible limit of the spectrum. With the exception of the well-known pair of lines of potassium, I am not aware that any lines in metallic spectra, which have been carefully studied, have been found below this limit, though recently, in the spectra of some of the rarer earths, I believe some few lines have been recorded.

Having photographed the emission spectra produced in the arc of several metals, it appears, so far as examination has been made, that only those which can be volatilised at a low temperature have any lines in the infra-red region. Sodium is an example of this. It has a pair of lines at wave-length of about 8187 and 8199 of an intensity of about 3, taking the intensity of D lines as 10. It will be noted that the difference in wave-length between this pair is greater than that of the D lines. They do not seem to have any corresponding dark lines in the solar spectrum, though there are three faint lines which lie close to these wave-lengths.

In the calcium spectrum there is a pair of very faint lines which lie between  $\lambda$  8500 and 8600. Their exact wave-lengths have not at present been determined.





